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EFFECT OF pH ON STRENGTH OF RESIN BONDS

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ADVANCE RESTRICTED REPORT

EFFECT OF pH ON STRENGTH OF RESIN BONDS

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INTRODUCTION

The increased use of resin-bonded plywood for structural parts of aircraft has made it necessary to determine the effect of various chemical properties of the resins on the strength properties of the resin bonds. Information of this nature is needed to utilize the materials properly in building satisfactory aircraft and to evaluate the causes of failures. Determination of the effect of acid on the strength and aging properties of various types of resin bonds is one important phase of this work. This report presents the results of an investigation which was made to determine these relationships.

The degree of acidity or hydrogen ion concentration can conveniently be reported as a pH value which is the logarithm of the reciprocal of the gram ionic hydrogen equivalents per liter; that is, pH = log $1/H^+$ per liter. Water has a concentration of H^+ ion of 10^{-7} and of OH^- ion of 10^{-7} moles per liter or a pH value of 7, and is said to be neutral in reaction. The presence of an acid in a water solution increases the concentration of hydrogen ions. Hence the concentration of hydrogen ions in an acid solution becomes 10^{-6}, 10^{-5}, or greater, and the pH value is less than 7. The presence of an alkali in a water solution increases the concentration of hydroxyl ions and decreases that of the hydrogen ions. Hence the concentration of hydrogen ions in an alkaline solution becomes 10^{-8}, 10^{-9}, or less, and the pH value is greater than 7. The product of the hydrogen ion concentration and the hydroxyl ion concentration is always equal to 10^{-14} in aqueous medium at 25° C. The pH value has been used throughout this report to indicate the degree of acidity of the various specimens.

The two most commonly used types of bonding agents in the manufacture of resin-bonded plywood are the phenol-formaldehyde and the urea-formaldehyde resins. Both types are cured either by the "hot-set" or the "cold-set" method.

Since the demarcation between "cold-set" and "hot-set" bonding resins has not been definitely established in the industry, the resins used in this project were classified according to the temperature required to cure the resin in a commercially practical period of time, as follows:

Class R. These resins do not require a higher degree of heat for curing than that available at ordinary room or factory conditions.

Class M. These resins require a degree of heat greater than that available at room or factory conditions, but not over 160° F (71° C).

Class H. These resins require a temperature greater than 160° F (71° C).

To obtain a satisfactory degree of cure of class R and some class M resins, it is necessary with most of the commercial resins to use very active catalysts. One of the most active catalysts for curing these types of resins is the hydrogen ion which is usually expressed in terms of pH units when the concentration is less than one molar.

It is an established fact that wood deteriorates rapidly in acidic media. It is also known that urea-formaldehyde resins are not as resistant to acid conditions as are phenolic resins. The work reported herein was designed to determine the effect of the pH of the resin bond on the strength properties of the resin-wood composite since the failures may be in the resin, in the wood, or in both resin and wood. It should be noted, however, that the acid conditions in the resin-bonded birch panels tested are attributable to the ingredients in the resin-glue mixtures and not to the wood or any extraneous source.

This investigation, conducted at the National Bureau of Standards, was sponsored by, and conducted with financial assistance from, the National Advisory Committee for Aeronautics.

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MATERIALS

A group of commercial resins which are being used to a great extent in the manufacture of resin-bonded plywood aircraft was selected for this work. The commercial designations and the manufacturers of the resins, and the classification of the various resins and resin-catalyst mixtures on the basis of the temperature required for curing, are given in table I.

The test panels were made with sliced birch veneers having an average thickness of 0.01 inch. The thin veneers were used to obtain a higher resin content than that normally used in aircraft plywood. Since the acidic conditions result from the resin, a high resin content would be expected to magnify the effect of the pH on the strength properties of the composite.

PREPARATION OF TEST PANELS

The resin glues were prepared according to directions received from the manufacturers and were applied to the birch veneers by means of rollers. This method produced resin films of uniform thickness on both sides of the veneers. The veneers coated with the class H resins were suspended from a drying rack and allowed to dry about 20 hours before assembling and pressing. The veneers coated with the class R and class M resins were assembled and pressed immediately after coating. Each panel consisted of 8 birch veneers arranged with the grain of plies 1, 3, 6, and 8 parallel to one another and with the grain of plies 2, 4, 5, and 7 perpendicular to the face plies. All the test panels were pressed at approximately 100 pounds per square inch.

The birch veneers used in each panel were conditioned at 77° F (25° C) and 50 percent relative humidity, and were weighed before the resin coating was applied. The completed test panel was also conditioned and weighed. The resin content of the test panel was then calculated by means of the following equation:

$$\text{Resin content, percent} = \frac{\text{wt. of test panel} - \text{wt. of conditioned veneers}}{\text{wt. of test panel}} \times 100$$

Three panels were prepared with each resin or resin-catalyst mixture. The panels made with class H resins were 12 by 12 inches in area; the panels made with class R and class M resins were 9 by 9 inches. The thickness of the test panels were approximately 0.08 inch. The conditions used to cure the panels, the average densities, and the average resin contents are given in table I. The densities were determined by weighing and measuring machined specimens.

TESTING PROCEDURE

Aging

Each test panel was cut into quarters and treated as follows:

1. One quarter section was not subjected to any aging treatment.

2. One quarter section was heated in a forced-draft oven at 176° F (80° C) for 40 hours.

3. One quarter section was subjected to a continuous oven-fog cyclic accelerated aging test. The cycle in this test consisted of the following:

Exposure period (hr)	Temperature (deg F)	Temperature (deg C)	Relative humidity (percent)	Apparatus
2	77	25	100	Fog cabinet
2	150	65	<5	Forced-draft oven
2	77	25	100	Fog cabinet
18	150	65	<5	Forced-draft oven

The sections were exposed for a total of 200 hours in the oven and 40 hours in the fog cabinet.

4. One quarter section was exposed on the roof of the Industrial Building on racks at an angle of 45° facing south. This exposure test is still in progress.

Determination of pH

A thin film of the resins of class R and class M was cast on glass and allowed to dry for 15 hours at a temperature of 70° to 79° F (21° to 26° C). The resin film was then removed from the glass and ground to a fineness of 40 mesh. Two grams of the powdered resin were suspended in 10 milliliters of distilled water and the pH of the suspension was measured by means of a glass electrode after 15 minutes, and after 24, 48, 72, and 96 hours. The pH values were constant after 72 hours.

Films were prepared from the class H resins by casting them upon a glass plate, using a knife blade to remove excess resin and make the thickness of the coating 0.02 inch or less. The cast films were placed in a circulating-air oven at 150° F (65° C) until examination showed that most of the solvent had evaporated; this process required about 4 hours except in the case of Plaskon 107, which was cured after 3 hours at 150° F (65° C) and was not subjected to any further heating. This drying was followed by a cure in the oven at 300° F (149° C) until the films were hard and brittle, the latter operation requiring about 30 minutes. The hard, brittle films were pulverized in a small rock-crushing mortar and passed through a 40-mesh screen. The pH values of the powdered films were measured in the same manner as those of the class R and the class M films.

The acidity of the test panels was determined by grinding a portion of the panel to 40 mesh in a Wiley mill and suspending 1 gram of the powder in 5 milliliters of distilled water. Measurements of pH were made after 24, 48, and 72 hours. The pH values of the water suspensions were constant after 48 hours.

The pH of the distilled water used in making the resin suspensions was 6.3. A few of the resin films and powdered panels were also suspended in dilute hydrochloric acid solution of pH 4.5. The pH values of the acid suspensions are reported in table II and did not differ appreciably from those of the water suspensions. All the pH measurements were made at a temperature of 77° F (25° C) with a glass electrode. The measurements reported are accurate to ±0.05 pH unit.

Strength Properties

The test specimens for determining the strength properties were cut from the quarter sections after the aging treatments. The specimens were machined and then conditioned at 77° F (25° C) and 50 percent relative humidity prior to testing. All the tests were made at 77° F (25° C) and 50 percent relative humidity.

The flexural modulus of elasticity was measured on an Olsen Stiffness Tester, Tour-Marshall design. Specimens 5 inches long and 0.5 inch wide were cut from the panels. Two measurements were made on each specimen, one on each end. The test span was 2 inches long; the total bending moment applied to the specimen was 3 inch-pounds. The angular deflections were plotted against the bending moments and the deflection at a stress of 2500 pounds per square inch was determined from the curve. The modulus of elasticity in flexure then was calculated from the approximate expression

$$E = \frac{229.2\ Pl^2}{D\ a\ h^3}$$

where

E modulus of elasticity in flexure

P load

l length of beam

D deflection, degrees

a width of beam

and

h thickness of beam.

This expression was derived from the formula for the deflection of a cantilever beam with a concentrated load at one end.

The flexural strength was measured on specimens 1.0 inch long and 0.75 inch wide cut from the panels. The specimen was supported on two parallel supports with a

span of 5/8 inch. The load was applied at the center of the span by a pressure piece similar to the supports. The edges of the support pieces and of the pressure piece were rounded to 1/8-inch radius. The tests were made on a hydraulic testing machine with a head speed of 0.05 inch per minute. The machine was accurate to 2 percent of the lowest applied load.

The impact tests were made on an Izod impact machine of 2 foot-pounds capacity. Specimens 2.5 inches long and 0.5 inch wide were cut from the panels.

The tensile tests were made according to the method described in section B-1 of Federal Specification L-P-406 for plastics. Type I specimens were used; the width of the reduced section was 0.5 inch. The tests were made on a hydraulic testing machine with self-alining Templin grips. The rate of head speed was 0.05 inch per minute.

Shear specimens 4 inches long and 0.75 inch wide were cut from the panels. A groove 1/8 inch wide and extending through approximately $4\frac{1}{2}$ veneers was milled on one face of the panel parallel to the 0.75-inch dimension. A similar groove was milled on the opposite face. The grooves on the specimens used in the preliminary tests were 1/2 inch apart, but, since many tensile failures were obtained, the distance between the grooves was reduced to 1/4 inch on the later specimens. The specimens were broken on a hydraulic testing machine at a rate of loading of 200 pounds per square inch per minute.

Delamination

One strip 0.5 inch wide cut from each quarter section of each test panel was subjected to a delamination test. The strips were placed in individual 3- by 20-centimeter test tubes which contained distilled water previously heated to the boiling point by immersion of the tubes in a water bath. The tubes containing the test strips were left in the bath of boiling water for 1 hour. On removal from the test tubes the specimens were immersed in water at 77° F (25° C) for 15 minutes and then dried at 140° F (60° C) in a forced-draft oven for 22 hours. This procedure constituted one cycle of the test. At the end of each cycle the test specimens were bent over a mandrel of 8-inch radius. After five cycles the specimens were bent over a 4-inch mandrel. Observations regarding delamination were made.

RESULTS OF TESTS

A preliminary investigation was made to obtain data for use in selecting the strength properties to be measured on all the test panels. Six panels were prepared with Tego film and six with Uformite 430 catalyzed with 10 percent ammonium chloride. These two materials were selected to determine the effects of high and low pH conditions, respectively. One-half of each panel was tested unaged and the other half was subjected to an aging test prior to measurement of the strength properties. The strength properties measured in these preliminary tests were flexural modulus of elasticity, and flexural, impact, tensile, and shear strengths. The results are given in table II.

On the basis of the results obtained in these preliminary tests, the size of the test specimens required, and an analysis of the stresses in the various tests, it was decided to employ the flexural, impact, and shear strengths for detecting the deterioration of the resin-bonded birch plywoods. The critical pH values in the acid range - that is, the pH value below which serious degradation of the plywood may occur because of free acid, observed for the urea-formaldehyde and phenol-formaldehyde resin-bonded panels in the various physical tests, are summarized for convenience in table III. Detailed results of the tests are presented in tables IV, V, VI, and VII. The results of the shear tests were not available at the time this report was prepared and will be presented in a subsequent report.

DISCUSSION OF RESULTS

Use of the various commercial resins with their catalysts selected for this investigation resulted in pH values for birch plywood ranging from 1.7 to 8.4. (See table I.) The pH values for the test panels made from the urea-formaldehyde materials ranged from 1.9 to 5.7; the pH values for the test panels made from the phenolic materials ranged from 1.7 to 8.4. Test panels were made also with a new resin, Laminac, which is neither a phenolic nor a urea-formaldehyde type. The pH values for the test panels made from Laminac ranged from 3.7 to 4.0.

The pH values of the birch plywood were not affected

by moderate baking or by exposure to cycles of heat and fog. This indicated that the acidic compounds determining the pH of the composite did not escape readily from the structure or did not react with the birch or its decomposition products in such a way that they lost their chemical identity. It would seem reasonable, therefore, to assume that the deterioration caused by pH would continue until failure occurred.

The results of the preliminary tests reported in table II indicated that the weakening of the resin-bonded birch plywoods was first evident in the flexural and impact strengths. Tentatively, the shear strength also appeared to be reduced early in aging treatments of the composite. In order to clarify this latter point, more data on shear strength are being obtained. The flexural modulus of elasticity and tensile strength did not appear to be markedly affected in short-time aging tests.

The flexural strength of the urea-formaldehyde resin-bonded birch plywood depended markedly on the pH of the composite. This is shown by the data in table IV and graphically in figures 1 and 2. These is apparently a critical pH value between 3.8 and 4.6 for birch plywood bonded with urea-formaldehyde resins, below which optimum flexural strengths are not obtained even on unaged material. The oven-aged specimens with pH values of 3.6 and less underwent a greater proportionate loss of strength than those with pH values of 3.8 and more. The oven-fog-aged specimens with pH values of 3.8 and less underwent, with one exception, a greater proportionate loss of strength than those with pH values of 4.6 and more. This indicates that if optimum strengths are desired and if these strengths are to be retained on aging, the pH of the composite should be greater than 3.8.

The flexural strength of the phenolic resin-bonded panels did not show an exact correlation with pH, but an examination of the values in tables IV and VII shows that the presence of acid catalyst causes a decrease in this property in the unaged panels in every case. This decrease was noticed especially with the panels prepared with the catabond resins 590 and 2000Z, wherein concentrated hydrochloric acid catalysts were used. It is well known that hydrochloric acid has a decidedly deleterious effect on most woods. There is apparently a critical pH value for the initial flexural strength of plywood bonded with phenolic resin between 3.1 and 3.6. Exposure to

both oven and oven-fog-aging treatments caused marked decreases in flexural strengths when the pH values were 3.1 or less. The critical limit of pH with respect to loss in strength on aging appears to be between 3.1 and 3.6 for the phenolic-resin-bonded birch panels.

The impact strength of the plywoods bonded with urea-formaldehyde resins was also found to be dependent on the pH. This is shown by the data in table V and graphically in figure 3. The critical value of the pH for the unaged specimens appears to be between 3.6 and 3.8. For the oven-aged and the oven-fog-aged specimens there appears to be a definitely greater loss in strength below a pH of 3.6, but the specimens of 3.6 and higher pH also showed appreciable loss in strength on aging. This indicates that the loss in impact strength on aging can be attributed to both deterioration of the wood at low pH and deterioration of the resin over the whole pH range investigated. It should be noted that Plaskon 700-2 is a modified urea-formaldehyde resin having some of the characteristics of a phenolic resin, which probably accounts for its greater initial impact resistance.

The impact strength of the plywood panels bonded with phenolic resins shows the same general relationship to pH as the flexural strength values. In each case, the presence of acid catalyst caused a decrease in strength. The lowest values were again obtained with the catabond resins catalyzed with hydrochloric acid. The critical pH value is apparently in the range between 3.1 and 3.6. The critical pH for the oven-aged specimens is between 2.7 and 3.1. The oven-fog-aged specimens with pH values of 3.1 and less underwent a greater proportionate loss in impact strength than those with pH values of 3.6 and more. Since the oven-fog-aging treatment is considered to simulate natural aging more closely than the continuous dry heat, the critical pH for the phenolic resin composites should be considered as in the range of 3.1 to 3.6 on the basis of the impact tests.

The failure of the urea-formaldehyde resin-bonded materials in the delamination test is also affected by the pH of the plywood. The critical pH value in this test appears to be between 3.8 and 4.6 for both the unaged and the aged specimens.

No failure of the phenolic resin-bonded composites occurred in the delamination test. The unaged and aged

specimens with pH values of 3.1 or less were brittle in the final flexibility test on the 4-inch mandrel. With one exception, those with pH values of 3.6 or more were flexible throughout this test.

The critical pH for the phenolic resins is not definitely established by the data in this report because phenolic resin films in the range of pH between 2.0 and 4.0 were not included in the tests. Further work is under way to establish closer limits on this critical pH. It is evident from the pH values obtained on the test panels that the pH of the resin-catalyst mixture will have to be such that the pH at the bond will be above 3.1. It appears, in general that birch wood is subject to serious deterioration when the pH at the bond is below about 3.5.

It is to be expected that there also will be a critical pH in the alkaline range above which resin-bonded birch would be subject to deterioration in strength. This point has not yet been established in the experimental work on this project.

CONCLUSIONS

1. The pH values of the birch plywoods are not markedly affected by moderate baking or by exposure to cycles of heat and fog.

2. The flexural and impact strengths, both initially and after aging, of birch plywoods bonded with urea-formaldehyde resins are definitely affected by the pH. The critical pH value, below which optimum strengths are not obtained and deterioration upon aging becomes appreciable, lies between 3.8 and 4.6.

3. The flexural and impact strengths, both initially and after aging, of birch plywoods bonded with phenolic resins are definitely affected by the pH. The critical pH value, below which optimum strengths are not obtained and deterioration upon aging becomes appreciable, lies between 3.1 and 3.6. Hydrochloric acid has a decidedly deleterious effect on plywoods made with phenolic resins.

4. The delamination of birch plywoods made with urea-formaldehyde resins is affected by the pH. The

lower the pH, the fewer cycles required for delamination to occur.

5. The delamination of birch plywoods made with phenolic resins is not affected by the pH. When the pH is 3.1 or less, the materials are not as flexible as those with pH values of 3.6 or more.

National Bureau of Standards,
Washington, D. C.
August 6, 1943.

TABLE I.- DESCRIPTION OF RESINS AND RESIN-BONDED BIRCH PANELS

Commercial Designation of Resins	Manufacturer	Catalyst Added to Resin	Classification[a]	Conditions of Cure: Temperature °F	Conditions of Cure: Time hr:min.	Density, Average g/cm³	Resin Content of Panel, Average %	pH of Resin Film	pH of Resin-Bonded Birch Plywood: Unaged	pH of Resin-Bonded Birch Plywood: Oven-Aged	pH of Resin-Bonded Birch Plywood: Oven-Fog-Aged
A. Urea-Formaldehyde Resins											
Uformite 430	Resinous Products and Chemical Co.	10% ammonium chloride	R	Room	24:0	0.91	33	1.2	1.9	---	---
Uformite 430	Resinous Products and Chemical Co.	10% "Z"	R	Room	24:0	0.94	37	1.6	2.0	2.1	2.6
Uformite 430	Resinous Products and Chemical Co.	10% "Y"	R	Room	24:0	0.94	40	1.8	2.4	2.5	3.3
Plaskon 201-2	Plaskon Div., Libbey-Owens-Ford Glass Co.	2% "A"	R	Room	24:0	0.93	37	2.6	3.2	3.4	3.3
Casco #5	Casein Company of America	5% "AA"	R	Room	24:0	1.02	37	3.2	3.4	3.1	3.6
Plaskon 250-2	Plaskon Div., Libbey-Owens-Ford Glass Co.	None	R	Room	24:0	0.88	34	3.4	3.6	3.4	3.6
Plaskon 107	Plaskon Div., Libbey-Owens-Ford Glass Co.	7% B-7	H	300	0:8	0.96	31	4.0	3.8	4.0	4.0
Plaskon 700-2	Plaskon Div., Libbey-Owens-Ford Glass Co.	16% modifier	M	{Room {150	20:0} 3:0}	0.96	35	4.8	4.6	4.6	4.6
Uformite 430	Resinous Products and Chemical Co.	None	H	300	0:6	1.00	33	7.7	4.6	4.6	4.7
Casco #5	Casein Company of America	None	H	300	0:30	0.98	35	7.5	5.7	6.0	5.9
B. Phenolic Resins											
Catabond 590	Catalin Corporation	11% hydrochloric acid (27.8%)	M	{Room {150	24:0} 1:0}	0.90	37	1.6	1.7	2.0	2.3
Durez 12041	Durez Plastics and Chemicals, Inc.	10% 7422	M M	150	24:0	0.97	36	1.4	1.8	1.8	1.9
Durez 11427	Durez Plastics and Chemicals, Inc.	10% 7422		150	24:0	1.04	25	1.4	1.8	1.8	1.9
Catabond 200-CZ	Catalin Corporation	11% hydrochloric acid (27.8%)	M	{Room {150	24:0} 3:0}	0.91	31	1.7	1.8	2.1	2.4
Bakelite XC-3931	Bakelite Corporation	3% XK - 2997	M	{Room {150	24:0} 2:0}	0.90	31	1.9	2.7	2.8	3.0
Bakelite XC-11749	Bakelite Corporation	45% XC - 11753	R	Room	24:0	0.87	31	1.9	3.1	3.0	3.3
Catabond 590	Catalin Corporation	None	H	300	0:30	0.94	29	3.8	3.6	3.7	3.6
Bakelite XC-11749	Bakelite Corporation	None	H	300	0:45	0.93	21	5.9	3.9	3.9	3.9
Bakelite XC-3931	Bakelite Corporation	None	H	300	0:30	0.97	35	5.5	4.5	4.7	4.5
Catabond 200-CZ	Catalin Corporation	None	H	300	0:30	1.00	37	6.6	4.6	4.6	4.7
Durez 12041	Durez Plastics and Chemicals, Inc.	None	H	300	0:30	0.97	33	8.2	5.0	5.0	5.0
Cascophen LT-67	Casein Company of America	8% M-18	M	150	24:0	0.95	37	7.5	6.4	6.2	6.2
Tego Film	Resinous Products and Chemical Co.	None	H	300	0:10	0.80	20	9.5	8.2	---	---
Amberlite PR-14	Resinous Products and Chemical Co.	None	H	300	0:12	0.85	28	9.8	8.4	8.3	8.0
C. Other Resins											
Laminac	American Cyanamid Company	1% benzoyl peroxide	H	{125 {300	0:30} 0:5 }	0.83	26	2.4	3.7	3.9	3.8
Laminac	American Cyanamid Company	1% lauroyl peroxide	H	{125 {300	0:30} 0:5 }	0.81	24	2.8	4.0	4.0	4.0

a. The resins are classified according to the temperature required to cure the resin. Class R includes those which cure quickly at room temperature. Class M includes those which require a temperature above room temperature but not over 160°F to cure. Class H includes those which require a temperature above 160°F to cure.

TABLE II.- RESULTS OF PRELIMINARY TESTS MADE ON RESIN-BONDED BIRCH PLYWOODS

Resin	Panel Designation	Density g/cm³	Resin Content %	pH In Acid[a]	pH In Water[a]	Tensile Strength Unaged Average Value lb/in²	Tensile Strength Unaged No. of Specimens	Tensile Strength Aged Average Value lb/in²	Tensile Strength Aged No. of Specimens	Tensile Strength Change in Strength %	Flexural Strength Unaged Average Value lb/in²	Flexural Strength Unaged No. of Specimens	Flexural Strength Aged Average Value lb/in²	Flexural Strength Aged No. of Specimens	Flexural Strength Change in Strength %	Flexural Modulus of Elasticity Unaged Average Value lb/in²	Flexural Modulus of Elasticity Unaged No. of Specimens	Flexural Modulus of Elasticity Aged Average Value lb/in²	Flexural Modulus of Elasticity Aged No. of Specimens	Flexural Modulus of Elasticity Change in Strength %
	Panels used for oven aging test																			
Tego film	Panel 1	0.79	20	8.0	8.1	13,000	2	13,000	2	0	19,400	1	18,200	2	-6	1,200,000	8	900,000	8	-25
Ditto	Panel 2	0.79	20	8.2	8.2	10,200	2	10,900	2	+7	20,000	2	17,600	2	-12	1,100,000	8	900,000	8	-18
	Panels used for oven-fog aging test																			
Ditto	Panel 3	0.80	20	8.3	8.4	13,300	2	13,700	2	+3	14,400	1	14,200	4	-1	800,000	8	900,000	8	+12
Ditto	Panel 4	0.81	20	8.2	8.1	11,700	2	12,400	2	+6	20,100	2	20,800	4	+3	1,200,000	8	1,400,000	8	+17
	Panels used for oven aging test																			
Uformite 430 with 10% ammonium chloride catalyst	Panel 1	0.93	33	1.9	1.9	7,200	2	6,200	2	-14	13,700	2	11,600	4	-15	1,300,000	4	1,100,000	8	-15
	Panel 2	0.91	33	1.9	1.9	6,200	2	4,800	2	-22	11,800	2	10,600	4	-10	1,200,000	4	900,000	8	-25
	Panels used for oven-fog aging test																			
Ditto	Panel 3	0.89	33	1.9	2.0	5,300	2	4,200	2	-21	14,200	2	8,400	8	-41	1,200,000	4	1,200,000	8	0
Ditto	Panel 4	0.89	31	1.9	2.0	5,700	2	5,500	2	-4	13,400	2	6,500	8	-51	1,400,000	4	1,400,000	8	0

Resin	Panel Designation	Density g/cm³	Resin Content %	pH In Acid[a]	pH In Water[a]	Izod Impact Strength, Unnotched, (Breaking Energy) Flatwise Unaged Average Value ft-lb	Flatwise Unaged No. of Specimens	Flatwise Aged Average Value ft-lb	Flatwise Aged No. of Specimens	Flatwise Change in Strength %	Edgewise Unaged Average Value ft-lb	Edgewise Unaged No. of Specimens	Edgewise Aged Average Value ft-lb	Edgewise Aged No. of Specimens	Edgewise Change in Strength %	Shear Strength Unaged Average Value lb/in²	Shear Strength Unaged No. of Specimens	Shear Strength Aged Average Value lb/in²	Shear Strength Aged No. of Specimens	Shear Strength Change in Strength %
	Panels used for oven aging test																			
Tego film	Panel 1	0.79	20	8.0	8.1	0.14	3	0.19	4	+36	0.23	4	0.27	4	+17	470	1	520	1	+11
Ditto	Panel 2	0.79	20	8.2	8.2	0.12	4	0.12	3	0	0.27	3	0.24	4	-11	740	1	420	1	-43
	Panels used for oven-fog aging test																			
Ditto	Panel 3	0.80	20	8.3	8.4	0.14	4	0.16	4	+14	0.27	4	0.25	4	-7	1200	1	650	2	-46
Ditto	Panel 4	0.81	20	8.2	8.1	0.18	4	0.13	4	-28	0.33	4	0.27	4	-18	530	1	900	2	+70
	Panels used for oven aging test																			
Uformite 430 with 10% ammonium chloride catalyst	Panel 1	0.93	33	1.9	1.9	0.11	2	0.09	4	-18	0.21	2	0.13	4	-38	200	1	190	2	-5
	Panel 2	0.91	33	1.9	1.9	0.10	2	0.09	4	-10	0.13	2	0.11	4	-15	200	1	210	2	+5
	Panels used for oven-fog aging test																			
Ditto	Panel 3	0.89	33	1.9	2.0	0.08	2	0.05	4	-38	0.14	2	0.07	4	-50	260	1	130	1	-50
Ditto	Panel 4	0.89	31	1.9	2.0	0.11	2	0.08	4	-27	0.16	2	0.15	4	-6	210	1	130	1	-38

a. The pH of the water used in these tests was 6.3; that of the dilute hydrochloric acid solution was 4.5. The pH of the water and dilute hydrochloric acid solution extracts of the birch veneers used in these tests was 4.6.

TABLE III.- SUMMARY OF CRITICAL pH VALUES FOR RESIN-BONDED BIRCH PLYWOOD[a]

Property	Critical value of pH in the acid range for resin-bonded birch plywood			
	Urea-formaldehyde resin bond		Phenolic resin bond	
	Critical pH of resin film is in the range:	Critical pH of unaged panel is in the range:	Critical pH of resin film is in the range:	Critical pH of unaged panel is in the range:
Flexural strength				
Unaged	4.0 to 4.8	3.8 to 4.6	1.9 to 3.8	3.1 to 3.6
Aged	4.0 to 4.8	3.8 to 4.6	1.9 to 3.8	3.1 to 3.6
Impact strength				
Unaged	3.4 to 4.0	3.6 to 3.8	1.9 to 3.8	3.1 to 3.6
	Critical over complte range tested		1.9 to 3.8	3.1 to 3.6
Delamination				
Unaged	4.0 to 4.6	3.8 to 4.6	No delamination. Brittle. 1.9 to 3.8	No delamination. Brittle. 3.1 to 3.6
Aged	4.0 to 4.6	3.8 to 4.6	No delamination. Brittle. 1.9 to 3.8	No delamination. Brittle. 3.1 to 3.6

[a]The critical pH is the pH below which serious degradation of the plywood may occur because of free acid.

TABLE IV.- EFFECT OF pH ON FLEXURAL STRENGTH OF RESIN-BONDED BIRCH PLYWOOD

Commercial Designation of Resins	Catalyst Added to Resin	Classification	pH of Unaged Panel	FLEXURAL STRENGTH: Unaged Panel: Average lb/in²	Unaged Panel: Range lb/in²	Unaged Panel: No. of Specimens	Oven-Aged Panel: Average lb/in²	Oven-Aged Panel: Range lb/in²	Oven-Aged Panel: No. of Specimens	Oven-Aged Panel: Change in Strength %	Oven-Fog-Aged Panel: Average lb/in²	Oven-Fog-Aged Panel: Range lb/in²	Oven-Fog-Aged Panel: No. of Specimens	Oven-Fog-Aged Panel: Change in Strength %
A. Urea-Formaldehyde Resins														
Uformite 430	10% ammonium chloride	R	1.9	13,200	10,800-15,500	12	11,100	9,900-12,800	8	-15.9	7,400	5,600-9,400	16	-43.9
Uformite 430	10% "Z"	R	2.0	14,300	11,300-15,600	12	12,600	11,100-15,000	12	-11.9	10,100	7,800-12,200	12	-29.4
Uformite 430	10% "Y"	R	2.4	15,800	14,600-17,400	12	13,900	11,500-15,600	11	-12.0	12,600	9,600-14,200	11	-20.2
Plaskon 201-2	2% "A"	R	3.2	18,400	16,900-19,800	12	17,200	15,800-18,900	12	-6.5	15,100	12,300-17,700	12	-17.9
Casco #5	5% "AA"	R	3.4	20,500	18,800-22,300	12	16,700	13,400-19,700	11	-18.5	15,700	12,200-20,700	12	-23.4
Plaskon 250-2	None	R	3.6	19,000	17,100-19,600	12	16,700	12,800-19,600	12	-12.1	16,000	15,200-17,700	12	-15.8
Plaskon 107	7% B-7	H	3.8	20,000	16,500-21,200	15	20,400	18,200-21,200	12	+2.0	17,200	16,000-20,400	12	-14.0
Plaskon 700-2	16% "modifier"	M	4.6	21,800	20,500-23,400	12	22,900	20,300-25,700	12	+5.0	21,300	15,900-24,800	12	-2.3
Uformite 430	None	H	4.6	22,700	20,700-25,700	15	22,800	19,500-27,400	15	+0.4	19,200	17,000-24,100	15	-15.4
Casco #5	None	H	5.7	23,100	19,300-26,600	13	23,000	19,600-25,600	15	-0.4	21,200	16,600-26,700	13	-8.2
B. Phenolic Resins														
Catabond 590	11% hydrochloric acid (27.8%)	M	1.7	10,500	6,800-12,700	12	11,100	8,700-12,500	12	+5.7	9,300	7,800-11,600	12	-11.4
Durez 12041	10% 7422	M	1.7	19,400	17,300-20,600	12	19,000	17,100-21,800	11	-2.1	13,500	10,100-15,300	12	-30.4
Durez 11427	10% 7422	M	1.8	20,200	16,700-21,800	12	18,200	15,100-20,500	12	-9.9	11,800	9,900-13,900	12	-41.6
Catabond 200-CZ	11% hydrochloric acid (27.8%)	M	1.8	11,700	8,800-17,400	12	13,100	10,800-16,900	12	+12.0	9,800	7,000-12,600	12	-16.2
Bakelite XC-3931	3% XK-2997	M	2.7	17,300	15,200-19,900	12	16,200	10,600-20,000	12	- 6.4	11,600	8,800-13,600	12	-32.9
Bakelite XC-11749	45% XK-11753	R	3.1	18,400	15,400-19,700	12	17,700	12,500-23,100	12	- 3.8	12,900	8,700-15,300	12	-29.9
Catabond 590	None	H	3.6	24,000	21,300-25,800	15	26,700	23,400-29,700	15	+11.2	21,700	18,100-25,200	15	-9.6
Bakelite XC-11749	None	H	3.9	24,600	22,100-26,800	15	27,900	23,300-29,700	15	+13.4	21,900	18,300-24,100	15	-11.0
Bakelite XC-3931	None	H	4.5	23,600	18,100-30,000	15	25,100	22,900-28,900	15	+6.4	24,800	23,300-26,300	15	+5.1
Catabond 200-CZ	None	H	4.6	24,000	21,300-25,800	15	26,500	23,000-29,200	15	+10.4	25,000	19,900-27,300	15	+4.2
Durez 12041	None	H	5.0	24,700	22,400-28,700	15	26,500	21,700-30,700	15	+7.3	23,800	21,300-27,100	15	-3.6
Cascophen LT-67	8% M-18	M	6.4	21,900	17,600-24,200	12	25,400	23,200-27,100	12	+16.0	21,900	19,100-24,100	12	0
Tego film	None	H	8.2	19,700	14,400-21,000	10	17,900	16,000-19,200	4	-9.1	17,500	13,900-21,700	8	-11.2
Amberlite PR-14	None	H	8.4	21,800	16,000-25,300	15	22,600	20,100-25,600	15	+3.7	20,500	18,600-24,400	15	-6.0
C. Other Resins														
Laminac	1% benzoyl peroxide	H	3.7	15,300	12,700-18,500	13	19,800	12,400-23,300	15	+29.4	17,800	16,900-19,600	12	+16.3
Laminac	1% lauroyl peroxide	H	4.0	18,800	17,000-21,000	15	19,500	15,000-20,700	15	+3.7	16,300	12,200-19,800	15	-13.3

TABLE V.- EFFECT OF pH ON IMPACT STRENGTH OF RESIN-BONDED BIRCH PLYWOOD

Commercial Designation of Resin	Catalyst Added to Resin	Classification	pH of Unaged Panel	IZOD IMPACT STRENGTH, UNNOTCHED (BREAKING ENERGY/THICKNESS) Unaged Panel Average Value ft-lb/in	Unaged Panel Range ft-lb/in	Unaged Panel No. of Specimens	Oven-Aged Panel Average Value ft-lb/in	Oven-Aged Panel Range ft-lb/in	Oven-Aged Panel No. of Specimens	Oven-Aged Panel Change in Strength %	Oven-Fog-Aged Panel Average Value ft-lb/in	Oven-Fog-Aged Panel Range ft-lb/in	Oven-Fog-Aged Panel No. of Specimens	Oven-Fog-Aged Panel Change in Strength %
A. Urea-Formaldehyde Resins														
Uformite 430	10% ammonium chloride	R	1.9	2.0	1.4-2.5	12	1.4	1.2-1.6	8	-30.0	1.3	0.8-1.8	8	-35.0
Uformite 430	10% "Z"	R	2.0	2.0	1.5-2.8	6	1.4	0.8-1.6	6	-30.0	1.2	0.9-1.6	6	-40.0
Uformite 430	10% "Y"	R	2.4	2.0	1.9-2.0	6	1.3	1.1-1.5	6	-35.0	1.5	1.4-1.8	6	-25.0
Plaskon 201-2	2% "A"	R	3.2	2.2	1.8-2.5	6	1.8	1.6-2.2	6	-18.2	1.8	1.1-3.0	6	-18.2
Casco 5	5% "AA"	R	3.4	2.2	2.0-2.4	6	1.4	1.1-1.6	6	-36.4	1.7	1.5-1.9	6	-22.7
Plaskon 250-2	None	R	3.6	2.2	1.8-2.8	6	1.6	1.4-1.8	6	-27.3	1.8	1.8-2.1	6	-18.2
Plaskon 107	7% "B-7"	H	3.8	2.8	2.6-3.1	18	2.8	2.7-2.9	18	0	2.3	2.2-2.3	18	-17.9
Plaskon 700-2	16% modifier	M	4.6	4.0	3.6-4.2	6	3.2	2.9-3.8	6	-20.0	2.5	2.1-2.7	6	-37.5
Uformite 430	None	H	4.6	3.0	2.8-3.3	18	2.6	2.5-2.9	18	-13.3	2.5	2.2-2.7	18	-16.7
Casco 5	None	H	5.7	3.0	3.0-3.2	15	2.8	2.7-3.0	13	-6.7	2.5	2.0-2.9	14	-16.7
B. Phenolic Resins														
Catabond 590	11% hydrochloric acid (27.8%)	M	1.7	1.3	1.2-1.5	6	0.7	0.5-0.8	6	-46.2	0.8	0.7-0.9	6	-38.5
Durez 12041	10% 7422	M	1.8	2.3	2.0-2.5	6	2.1	1.6-2.7	6	- 8.7	1.6	1.2-1.8	5	-30.4
Durez 11427	10% 7422	M	1.8	3.0	2.5-3.5	6	2.0	1.8-2.1	6	-33.3	1.3	0.9-2.0	6	-56.7
Catabond 200-CZ	11% hydrochloric acid (27.8%	M	1.8	1.4	1.3-1.6	6	1.2	0.9-1.5	6	-14.3	1.1	0.9-1.2	6	-21.4
Bakelite XC-3931	3% XK-2997	M	2.7	2.2	2.0-2.4	6	1.4	1.3-1.6	6	-36.4	1.5	1.4-1.5	6	-31.8
Bakelite XC-11749	45% XK-11753	R	3.1	2.0	1.9-2.3	6	2.0	1.6-2.7	6	0	1.3	1.2-1.5	6	-35.0
Catabond 590	None	H	3.6	3.4	3.2-3.6	17	3.4	3.3-3.5	18	0	2.9	2.8-3.1	18	-14.7
Bakelite XC-11749	None	H	3.9	2.6	2.4-2.9	18	3.1	2.9-3.2	18	+19.2	2.5	2.1-2.9	18	- 3.9
Bakelite XC-3931	None	H	4.5	3.2	3.1-3.3	18	3.4	2.5-3.6	18	+6.2	2.8	2.7-3.0	18	-12.5
Catabond 200-CZ	None	H	4.6	3.5	3.2-3.6	18	3.8	3.7-3.9	18	+8.6	3.0	3.0-3.1	18	-14.3
Durez 12041	None	H	5.0	3.3	3.1-3.4	18	3.4	3.3-3.5	18	+3.0	2.7	2.3-3.4	18	-18.2
Cascophen LT-67	8% M-18	M	6.4	2.7	2.4-3.0	6	2.6	1.9-3.9	6	-3.7	2.3	2.0-2.3	6	-14.8
Tego film	None	H	8.2	3.0	2.5-3.7	23	2.8	2.6-3.0	8	-6.7	2.9	2.8-2.9	8	-3.3
Amberlite PR-14	None	H	8.4	3.0	2.7-3.4	18	3.6	2.9-3.7	18	+20.0	3.0	2.9-3.2	18	0
C. Other Resins														
Laminac	1% benzoyl peroxide	H	3.7	3.9	3.7-4.2	18	4.0	3.8-4.1	18	+2.6	3.6	3.3-4.0	18	-7.7
Laminac	1% lauroyl peroxide	H	4.0	4.7	4.4-5.1	18	4.8	3.5-3.8	18	+2.1	4.2	3.6-4.7	18	-16.4

TABLE VI.- EFFECT OF pH ON DELAMINATION OF RESIN-BONDED BIRCH PLYWOOD

Commercial Designation of Resin	Catalyst Added to Resin	Classification	pH of Unaged Panel	Condition of Specimen after Delamination Test[a]		
				Unaged Panel	Oven-Aged Panel	Oven-Fog-Aged Panel
A. Urea-Formaldehyde Resins						
Uformite 430	10% "Z"	R	2.0	D(1)	D(2)	D(1)
Uformite 430	10% "Y"	R	2.4	D(1)	D(2)	D(2)
Plaskon 201-2	2% "A"	R	3.2	D(3)	D(4)	D(3)
Casco 5	5% "AA"	R	3.4	D(2)	D(2)	D(2)
Plaskon 250-2	None	R	3.6	D(2)	D(4)	D(2)
Plaskon 107	7% "B-7"	H	3.8	D(3)	D(4)	D(3)
Plaskon 700-2	16% modifier	M	4.6	ND;F(5)	ND;F(5)	ND;F(5)
Uformite 430	None	H	4.6	SD(1); F(5)	SD(1); F(5)	SD(1): F(5)
Casco 5	None	H	5.7	SD(1) F(5)	D(1)	D(1)
B. Phenolic Resins						
Catabond 590	11% hydrochloric acid (27.8%)	M	1.7	ND;B(5)	ND;B(5)	ND;B(5)
Durez 12041	10% 7422	M	1.8	ND;B(5)	ND;B(5)	ND;B(5)
Durez 11427	10% 7422	M	1.8	ND;B(5)	ND;B(5)	ND;B(5)
Catabond 200-CZ	11% hydrochloric acid (27.8%)	M	1.8	ND;B(5)	ND;B(5)	ND;B(5)
Bakelite XC-3931	3% XK-2997	M	2.7	ND;B(5)	ND;B(5)	ND;B(5)
Bakelite XC-11749	45% XK-11753	R	3.1	ND;B(5)	ND;B(5)	ND;B(5)
Catabond 590	None	H	3.6	ND;F(5)	ND;F(5)	ND;F(5)
Bakelite XC-11749	None	H	3.9	ND;F(5)	ND;F(5)	ND;F(5)
Bakelite XC-3931	None	H	4.5	ND;F(5)	ND;F(5)	ND;F(5)
Catabond 200-CZ	None	H	4.6	ND;F(5)	ND;F(5)	ND;F(5)
Durez 12041	None	H	5.0	ND;F(5)	ND;F(5)	ND;F(5)
Cascophen LT-67	8% M-18	M	6.4	ND;F(5)	ND;F(5)	ND;B(5)
Amberlite PR-14	None	H	8.4	ND;F(5)	ND;F(5)	ND;F(5)
C. Other Resins						
Laminac	1% benzoyl peroxide	H	3.7	SD(1); F(5)	SD(1); F(5)	SD(1); F(5)
Laminac	1% lauroyl peroxide	H	4.0	SD(1); F(5)	SD(1); F(5)	SD(1); F(5)

[a]The specimens were subjected to 5 cycles of immersion in boiling water and drying, described on page 8 . Figure in parenthesis refers to cycle in which observation was made. Abbreviations are as follows:

D = delaminated
SD = slightly delaminated
ND = no delamination
B = brittle
F = flexible

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TABLE VII.-- EFFECT OF CATALYST ON FLEXURAL AND IMPACT STRENGTHS OF RESIN-BONDED BIRCH PLYWOOD

Commercial Designation of Resin	Catalyst Added to Resin	pH of Unaged Panel	Loss in Flexural Strength[a]			Loss in Izod Impact Strength[a]		
			Unaged Panel	Oven-Aged Panel	Oven-Fog-Aged Panel	Unaged Panel	Oven-Aged Panel	Oven-Fog-Aged Panel
			%	%	%	%	%	%
A. Urea-Formaldehyde Resins								
Uformite 430	None	4.6	---	---	---	---	---	----
	10% "Y"	2.4	30	39	34	33	50	40
	10% "Z"	2.0	37	45	47	33	46	52
	10% Ammonium Chloride	1.9	42	51	61	33	46	48
Casco 5	None	5.7	---	---	---	----	---	----
	5% "AA"	3.4	11	27	26	27	50	32
B. Phenolic Resins								
Catabond 590	None	3.6	---	---	---	----	---	----
	11% Hydrochloric Acid (27.8%)	1.7	56	51	57	62	79	72
Durez 12041	None	5.0	---	---	---	----	---	----
	10% 7422	1.8	21	28	43	30	38	41
Catabond 200-CZ	None	4.6	---	---	---	----	---	----
	11% Hydrochloric Acid (27.8%)	1.8	51	51	61	60	68	63
Bakelite XC-11749	None	3.9	---	---	---	----	---	----
	45% XK-11753	3.1	25	37	41	23	36	48
Bakelite XC-3931	None	4.5	---	---	---	----	---	----
	3% XK-2997	2.7	27	35	53	31	59	46

[a] Decrease in strength for the unaged, oven-aged, and oven-fog-aged panels, respectively, is calculated on the basis of the strength of the unaged, oven-aged, and oven-fog-aged panels, respectively, made without catalyst.

Urea-formaldehyde resin

	Resin	Catalyst
1,	Uformite 430	10% NH_4Cl
2,	Uformite 430	10% Z
3,	Uformite 430	10% Y
4,	Plaskon	10% A
5,	Casco 5	5% AA
6,	Plaskon 250-2	None
7,	Plaskon 107	7% B-7
8,	Uformite 430	None
9,	Plaskon 700-2	16% Modifier
10,	Casco 5	None

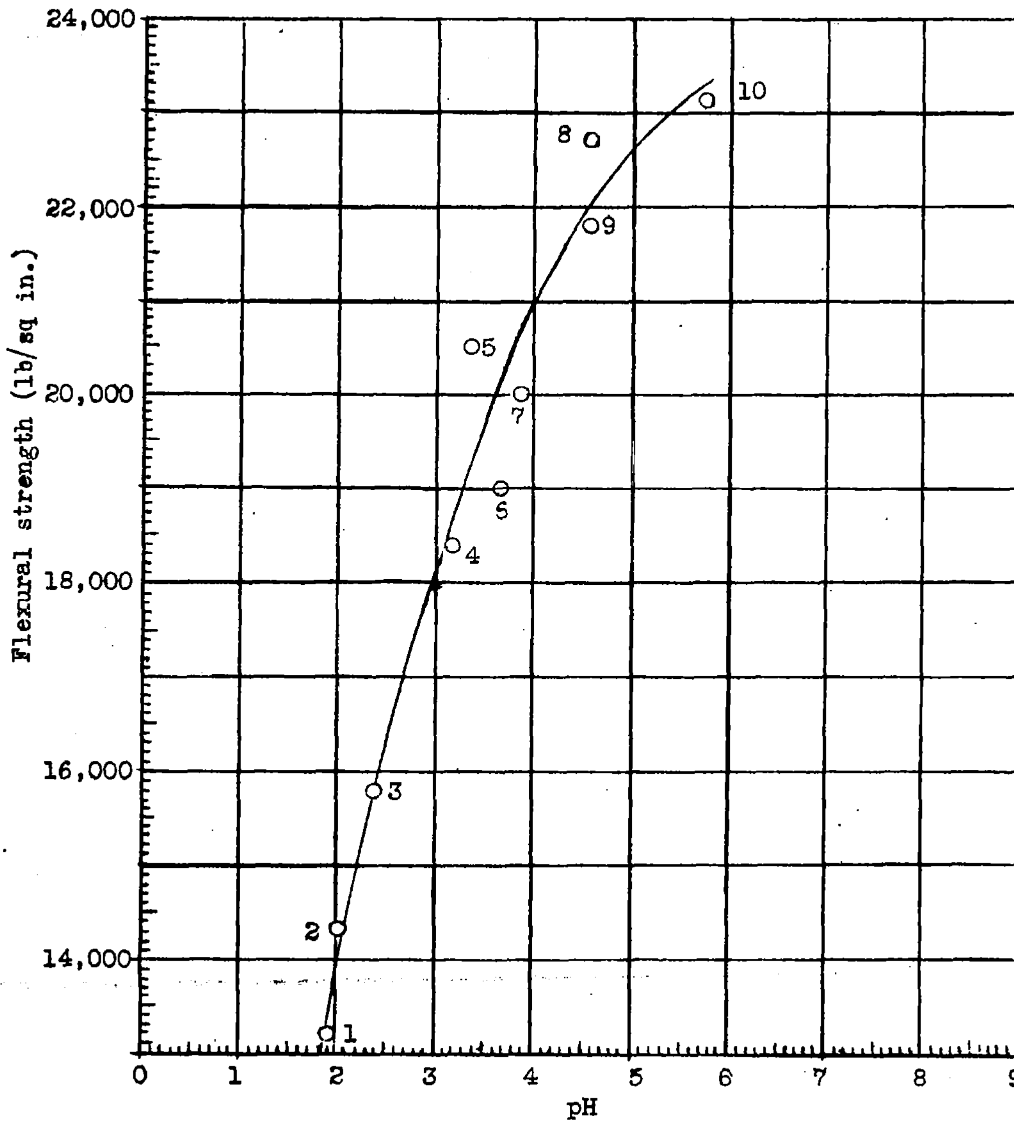

Figure 1.

W-46

Urea-formaldehyde
resin

Resin	Catalyst
1, Uformite 430	10% NH_4Cl
2, Uformite 430	10% Z
3, Uformite 430	10% Y
4, Plaskon	10% A
5, Casco 5	5% AA
6, Plaskon 250-2	None
7, Plaskon 107	7% B-7
8, Uformite 430	None
9, Plaskon 700-2	16% Modifier
10, Casco 5	None

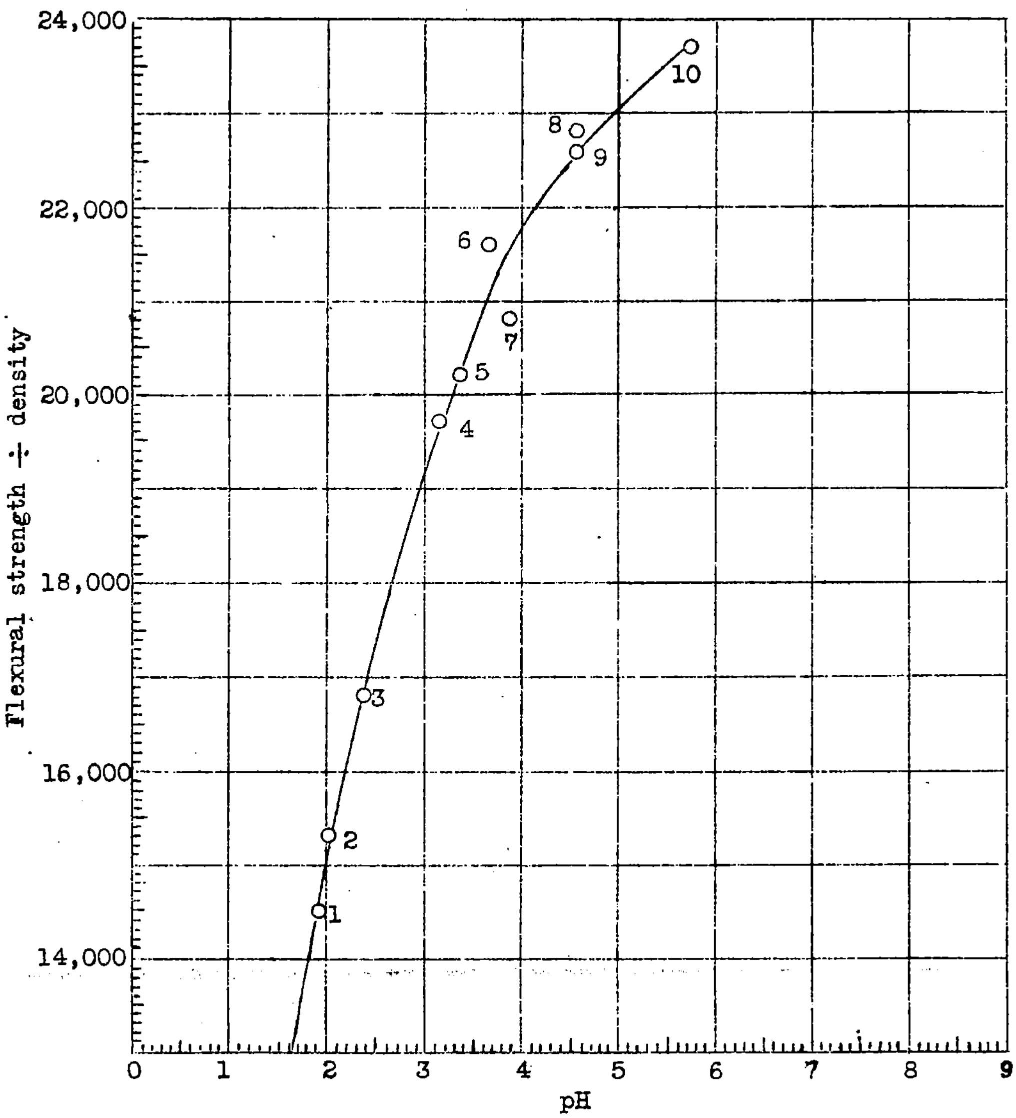

Figure 2.

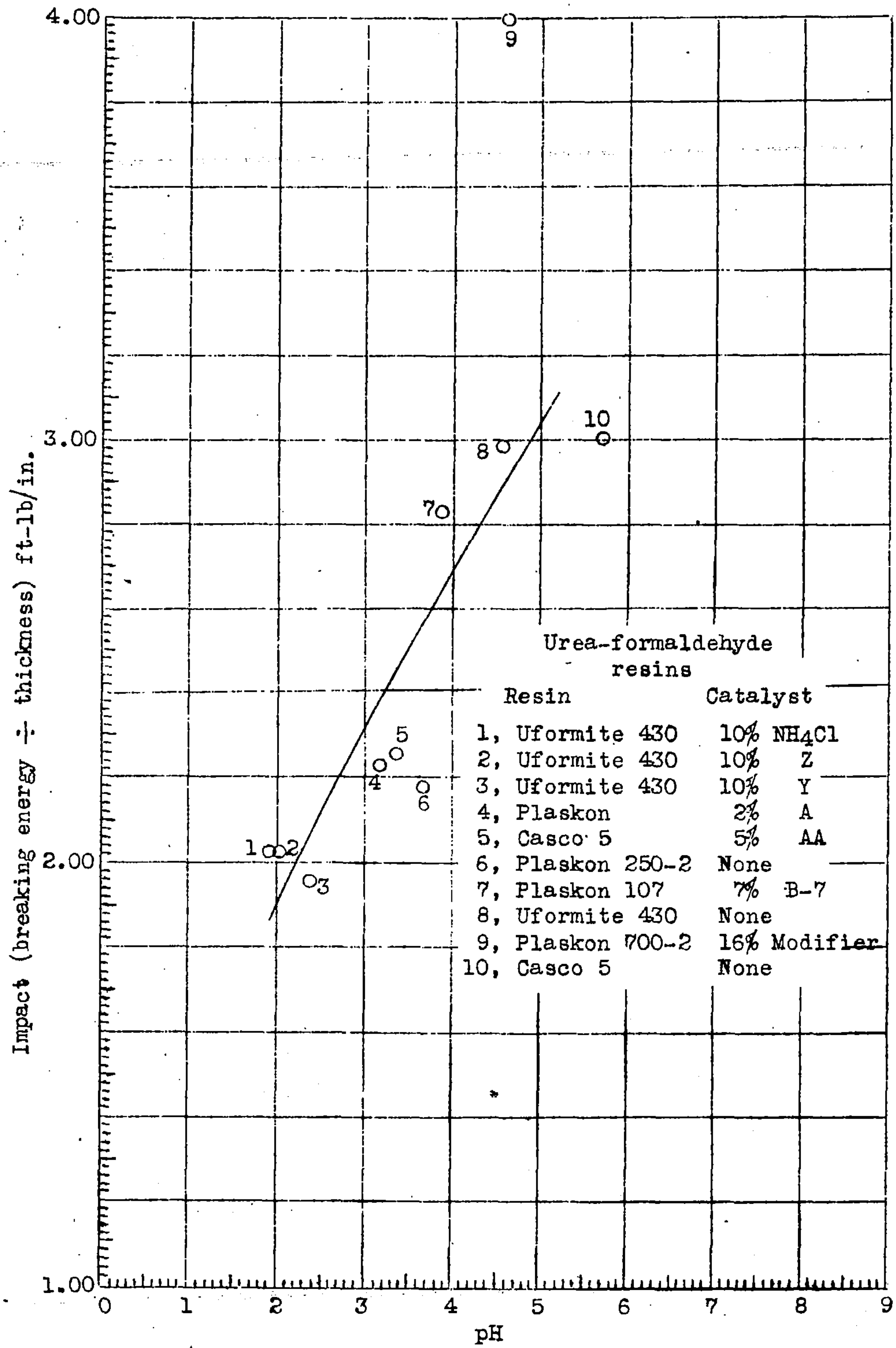
4.00
3.00
2.00
1.00
0
1
2
3
4
5
6
7
8
9
Impact (breaking energy ÷ thickness) ft-lb/in.
pH
1
2
3
4
5
6
7
8
9
10
Urea-formaldehyde resins
Resin Catalyst
1, Uformite 430 10% NH_4Cl
2, Uformite 430 10% Z
3, Uformite 430 10% Y
4, Plaskon 2% A
5, Casco 5 5% AA
6, Plaskon 250-2 None
7, Plaskon 107 7% B-7
8, Uformite 430 None
9, Plaskon 700-2 16% Modifier
10, Casco 5 None

Figure 3.